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An *ab initio* investigation of Cu_2Se and Cu_4Se_2

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Summary. Experimentally known copper selenium clusters show extraordinary geometrical features, especially short Cu–Cu distances. We report the first theoretical investigation of Cu_2Se and Cu_4Se_2. Various quantum chemical methods (SCF, MP2, CPF, CCSD, CCSD(T), LDF) are applied to determine the importance of dynamic electron correlation. We find that inclusion of correlation does not essentially change the electronic structure of the clusters but has a strong influence on geometries. To reduce the computational effort we apply effective core potentials (ECPs) in combination with small, but carefully optimized basis sets. The applicability of simple modellings of correlation energies for approximate inclusion of correlation effects in SCF geometry optimizations is tested.

Key words: Copper–selenium clusters – Cu_2Se–Cu_4Se_2 – *Ab initio* – Effective core potentials

1 Introduction

Ligand stabilized copper selenium clusters $Cu_{2n-x}Se_n(PR_3)_m$ with $n \geqslant 13$ have been recently synthesized and structurally characterized by Fenske et al. [1]. Three of these clusters have the stoichiometric composition $(Cu_2Se)_n$ which should be expected by simple valence considerations (d^{10} configuration of Cu^I). Exceptional but typical of these clusters are short Cu–Cu distances (down to 240 pm) and small Cu–Se–Cu angles (below 70°). The clusters show a tendency to form copper aggregations surrounded by selenium and stabilizing ligands at the outer surface.

A theoretical treatment of such clusters first of all requires a systematic investigation of the smallest unit Cu_2Se and the first few oligomers to clarify methodological questions. This concerns mainly two aspects: the importance of electron correlation, i.e. the applicability of various quantum chemical methods, and the choice of basis sets. Careful optimization of as small as possible basis sets and usage of effective core potentials (ECPs) are a prerequisite for calculations on larger clusters.

In the first section we briefly describe methods and programs used for the calculations. Basis sets and their optimization are discussed in the second section. We present the geometries of the clusters in the third section and discuss in more detail the bonding situation in Cu_2Se. Finally we consider an approach based on the incrementation of self consistent field (SCF) energy gradients by approximate (empirical) correlation contributions (SCF $+\ \Delta g$ method [2]) which paves the way to the treatment of larger clusters at the expense of SCF calculations.

2 Methods

SCF and second-order Møller–Plesset [3] (MP2) geometry optimizations were performed with the program package TURBOMOLE [4]. Force constants were calculated to check for local minima: analytical second derivatives on the SCF level and finite differences on the MP2 level. Basis sets were optimized for atoms and partly for molecules. Coupled-cluster singles-and-doubles [5] (CCSD) calculations including a perturbational estimate for triples [6] (CCSD(T)) were carried out with the program system ACES II [7] and Coupled Pair Functional [8] (CPF) calculations with the COLUMBUS [9] package (in its Karlsruhe version). Furthermore we performed Local Density Functional [10] (LDF) calculations using the DMol program [11].

The calculations performed in the course of this work were done on IBM RISC/6000 (TURBOMOLE, ACES II), IBM 3090 (COLUMBUS) and SGI 4D (DMol) computers.

3 Basis sets

With regard to future calculations on larger clusters, ECPs and corresponding basis sets were applied. For the copper atom we used an ECP for 10 core electrons developed by Dolg [12] and a relativistically corrected ECP for 18 core electrons given by Hurley et al. [13]. A relativistically corrected ECP for 28 core electrons was used for selenium [13].

The basis sets are listed in Table 1. Basis A is of type (8,7,6)/[6,5,3] for Cu (Ref. [12]) and (3,3,1)/[3,3,1] for Se (Ref. [13], augmented with a *d* function). For the CPF calculations we extended basis A by two *f* sets at Cu and two *d* sets (instead of one in basis A) and one *f* set at Se, resulting in (8,7,6,2)/[6,5,3,2] for Cu and (3,3,2,1)/[3,3,2,1] for Se (basis B). Basis C ((4,2,5)/[3,2,3] for Cu, (3,3,1)/[3,3,1]

Table 1. Basis sets used for ab initio calculations. n_{core} denotes the number of core electrons included in the ECP

Basis	Atom	n_{core}	Contraction pattern *s*/*p*/*d*	Origin
A	Cu	10	311111/22111/411	Ref. [12]
	Se	28	111/111/1	Ref. [13], + *d*(0.385)
B	Cu	10	311111/22111/411/11	Ref. [12], + 2*f*(4.962, 1.221)
	Se	28	111/111/11/1	Ref. [13], + 2*d*(0.6668, 0.2223) + *f*(0.38)
C	Cu	18	211/11/311	Ref. [13], contracted + 2*p*(0.15, 0.05)
	Se	28	111/111/1	Ref. [13], + *d*(0.385)
D	Cu	18	21/11/41	this work (see Table 2)
	Se	28	21/21/1	this work (see Table 2)

for Se) involves the same Se set as basis A, the Cu basis was taken from Ref. [13] with two additional *p* functions describing the 4*p* AOs.

Basis D ((3,2,5)/[2,2,2] for Cu, (3,3,1)/[2,2,1] for Se, see Table 2) was obtained by optimization of the atomic basis sets on the restricted Hartree–Fock (RHF) SCF level and a subsequent MP2 optimization of polarization functions simultaneously with the geometry of Cu_2Se. The atomic basis sets have the same quality as

Table 2. Cu and Se basis sets for use with ECPs with 18 core electrons at Cu and 28 core electrons at Se (basis D). The basis sets were optimized for the atomic ground states on RHF-SCF level. Subsequently polarization functions were optimized simultaneously with the structure of Cu_2Se on MP2 level

Type	Cu		Se	
	exponent	coefficient	exponent	coefficient
s	0.766999	− 0.197343	1.141219	− 0.616986
	0.118837	0.526739	0.550272	0.779448
	0.040349		0.161641	
p	0.949685		2.142918	0.058818
			0.384485	− 0.582536
	0.176665		0.119027	
d	47.361655	0.033066	0.310270	
	13.016504	0.169832		
	4.309976	0.385564		
	1.390545	0.460892		
	0.381137			

Table 3. Geometries obtained for Cu_2Se

Method	Basis[a]	r_{CuSe} [pm]	R_{CuCu} [pm]	∠CuSeCu [°]
SCF	A	228.1	334.1	94.2
	C	227.7	328.9	92.5
	D	227.2	313.4	87.2
MP2	A	220.0	262.1	73.1
	B	217.1	253.1	71.3
	C	220.5	248.2	68.5
	D	220.0	252.1	69.9
LDF	DNP[b]	219.7	243.1	67.2
CPF	B	221.9	262.1	72.4
CCSD	A	223.6	273.1	75.3
	C	223.3	257.2	70.3
CCSD(T)	A	223.6	259.7	71.0
	C	223.3	248.1	67.5
	D	222.4	251.8	69.0
SCF + Δg	D	222.4	251.7	68.9

[a] as described in Table 1

[b] Double numeric with polarization functions

the valence part of the split valence (SV) and double zeta (DZ) basis sets from Ahlrichs et al. [14]. Of great importance for the MP2-structure of Cu_2Se are the p-functions at Cu, much more than the d-function at Se. It turned out that for an accurate description of both polarization and correlation effects two p-functions are necessary for Cu. With only a single valence p at Cu, optimization resulted basically in a better description of the $4p$ AO near the nucleus only, and the resulting MP2-geometry was close to the SCF-geometries given in Table 3. Further optimization of basis D for the D_{4h} isomer of Cu_4Se_2 gave only minor changes of basis and geometry (at most 3% for the flat p-exponent and 0.2 pm for the Cu–Cu distance).

Comparing the geometries obtained with basis A and C on various theoretical levels (Table 3) shows that an ECP including 18 core electrons is sufficient for Cu. The influence on the Cu–Se distance is less than 1 pm and the change of the Cu–Se–Cu angle of 2–5° does not essentially affect the quality of the geometry, since – as will be seen later – this mode is very floppy anyway.

4 Structures

4.1 Cu_2Se

Cu_2Se (Fig. 1) is nonlinear with structural parameters depending strongly on the inclusion of dynamic electron correlation. The geometries obtained with various methods and basis sets are listed in Table 3. Within the SCF approximation we find a bond angle of about 93° which is in agreement with the intuitive picture of Cu–Se single bonds, i.e. an angle of 90° at Se. Inclusion of electron correlation reduces the angle to about 70° (i.e. a shortening of the Cu–Cu distance by about 60 pm), virtually independent of the method (MP2, CPF, CCSD, CCSD(T), LDF). Although there should be a slight Coulomb repulsion between the Cu atoms (vide infra) the short Cu–Cu distance is not unusual. In trinuclear Cu complexes one finds Cu–Cu distances down to 235 pm which has been attributed to attractive d^{10}–d^{10} dispersion type interactions [2]. The Cu–Se distance is shortened by 5–8 pm (depending on the method and the basis set employed) to about 222 pm by effects of electron correlation. This all together indicates the MP2 method to be sufficiently accurate in this case.

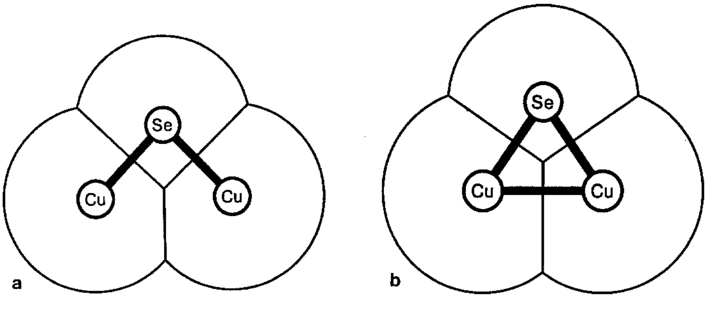

Fig. 1. Structure of Cu_2Se on (**a**) SCF and (**b**) CCSD(T) level

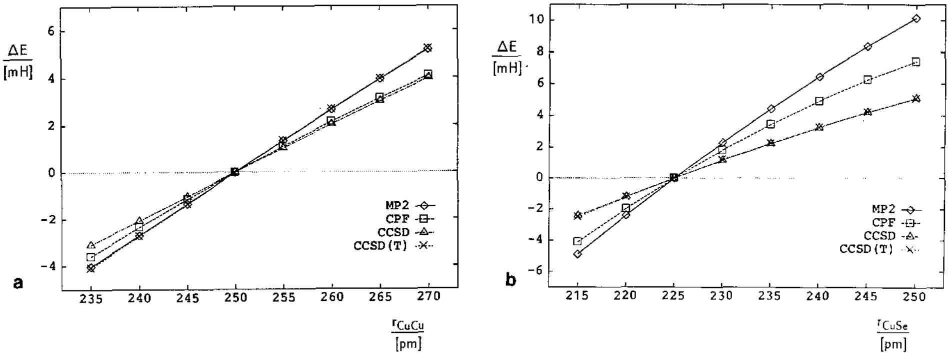

Fig. 2. Correlation energy in Cu_2Se as function of the (**a**) Cu–Cu and (**b**) Cu–Se distance. The MP2, CCSD and CCSD(T) results refer to basis D, the CPF results were obtained with basis B. Energies are given relative to the energy E_0 at (**a**) $r_{\mathrm{CuCu}} = 250$ pm and (**b**) $r_{\mathrm{CuSe}} = 225$ pm for the respective method, i.e. $\Delta E = E - E_0$

LDF as the most cost efficient method yields a somewhat too short Cu–Cu distance, especially as compared to the MP2, CPF and CCSD(T) calculations with large basis sets. Since relativistic effects which normally tend to shorten bond lengths (e.g. 4 pm for Cu_2 on CPF level [2]) are not implemented in DMol, there is a certain amount of error compensation for the bond lengths. With inclusion of relativistic effects (e.g. in ECPs, as done with the other methods) the distances should be even shorter.

For a direct comparison of various methods we have plotted the correlation energy in Cu_2Se with respect to variation of the Cu–Cu and Cu–Se distances (Fig. 2). Since it is the energy gradient (not the absolute energy) which determines the geometry, we have chosen a common reference point for the curves to get a direct comparison of their slopes.

For the Cu–Cu coordinate (Fig. 2a) it is striking that MP2 yields the same results as CCSD(T), while the CCSD and CPF curves are slightly more shallow (i.e. the latter two methods yield larger Cu–Cu distances). This can be rationalized as follows. MP2 often overestimates the effect of double excitations and therefore, higher order perturbation theory (MP3, SDQ-MP4) or infinite-order methods including only single and double excitations (CCSD, QCISD, CPF) predict slightly smaller correlation effects than MP2. CCSD(T) on the other hand introduces triple excitations in addition which often tend to enlarge correlation effects, thus leading to a close agreement of MP2 and CCSD(T) due to a fortuitous compensation of errors (at the MP2 level).

For the Cu–Se coordinate the shapes of the CCSD and CCSD(T) curves are almost identical (Fig. 2b). Thus double excitations appear to be sufficient for a correct description of the Cu–Se single bond. CPF and especially MP2 slightly overestimate correlation effects in this case.

Figure 3 shows the CCSD(T) energy hypersurface of Cu_2Se. It is very shallow along the Cu–Cu coordinate (MP2 force constant ≈ 0.015 a.u. ≈ 23 N/m*) as opposed to the Cu–Se coordinate (MP2 force constant ≈ 0.12 a.u. ≈ 187 N/m*). This is in line with the intuitive picture of chemical bonds between Cu and Se and

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* 1 a.u. = 1556.9 N/m; 1 N/m = 10^{-2} mdyn/Å

only weak interactions between the Cu atoms. The appreciable effect of correlation on structural parameters is mainly due to the small Cu–Cu force constant. The SCF energy increases by only 14 kJ/mol in going from the SCF to the CCSD(T) equilibrium structure, thus indicating only slight changes in the electronic structure.

At a Cu–Cu distance of 250–260 pm, as obtained with all correlation including methods, direct Cu–Cu interactions may begin to matter. This is confirmed by population analyses (PAs) of the SCF wave function. A PA based on occupation numbers (Roby–Davidson–PA [15] as modified by Ahlrichs and Ehrhardt [16]) gives a shared electron number (SEN) of 0.39 for the molecular orbital (MO) $19a_1$ (Fig. 4, the notation refers to symmetry group C_{2v} and inclusion of all electrons) and a total Cu–Cu SEN of 0.24. This MO is essentially the bonding linear combination of the Cu 4*s* atomic orbitals (AOs) and the Se $4p_z$ AO, further stabilized by admixture of $4p_x$ AOs at Cu. A qualitative diagram of the bonding situation is shown in Fig. 5.

The importance of dynamic electron correlation is reflected by the CCSD singles and doubles amplitudes. Their maximum values are 0.11 for single and 0.057 for double excitations. In our judgement these amplitudes are small enough

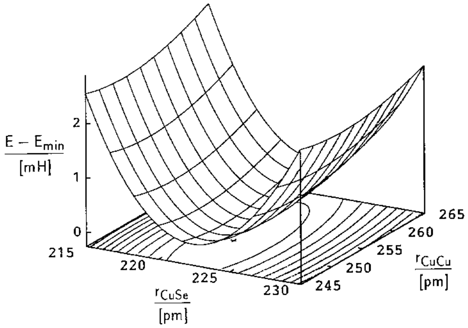

Fig. 3. CCSD(T) energy hypersurface of Cu_2Se. The shallowness along the r_{CuCu} coordinate is obvious

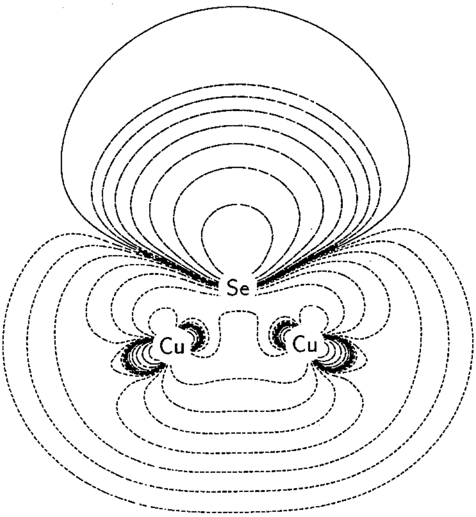

Fig. 4. Contour plot of the highest occupied Cu–Cu bonding MO $19a_1$ of Cu_2Se.

to justify a single reference treatment. There is also no pronounced preference of certain configurations which would suggest a multi-reference case. The most important amplitudes involve admixture of Cu–Cu bonding and Cu–Se antibonding MOs and thus support the idea of weak Cu–Cu interactions.

4.2 Cu_4Se_2

For the dimer Cu_4Se_2 we found three stable isomers (Figs. 6–8), in the following characterized by their point groups C_{2v}, C_{2h} and D_{4h}. A comparison of geometries and relative stabilities obtained with various methods is given in Tables 4–7. With inclusion of electron correlation the C_{2v} isomer is the most stable one, followed by the C_{2h} and D_{4h} isomers (Table 7). On the SCF level the C_{2v} isomer is higher in energy than the C_{2h} isomer. Comparing the C_{2v} structures obtained with SCF and correlation including methods (Fig. 6a, b) it is striking that the Cu_1–Cu_2 distance is much larger in the SCF case (480 pm versus 260 pm, see Table 4). As with the momoner this is a very weak mode (MP2 force constant ≈ 0.010 a.u. ≈ 16N/m) and only inclusion of electron correlation allows a close approach of Cu atoms

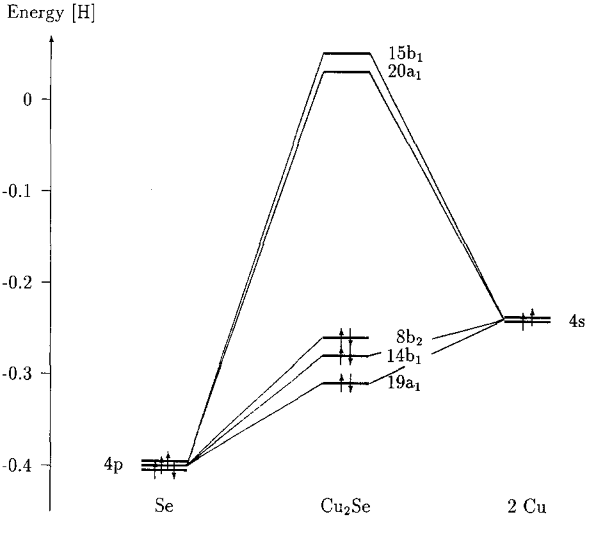

Fig. 5. MO scheme of the bonding situation in Cu_2Se (symmetry C_{2v})

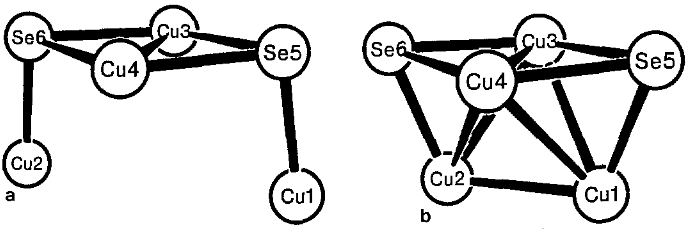

Fig. 6. Structure of the C_{2v} isomer of Cu_4Se on (**a**) SCF and (**b**) CCSD(T) level

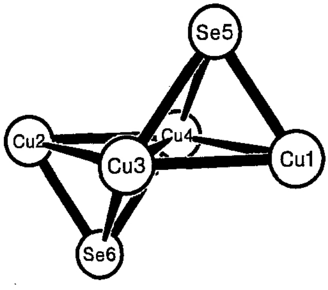

Fig. 7. Structure of the C_{2h} isomer of Cu_4Se_2 (CCSD(T))

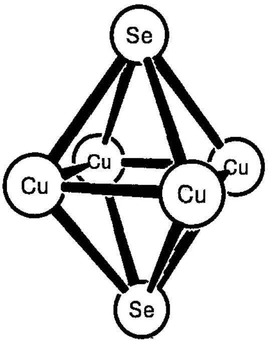

Fig. 8. Structure of the D_{4h} isomer of Cu_4Se_2 (CCSD(T))

Table 4. Geometries obtained for the C_{2v} isomer of Cu_4Se_2

Method	Basis[a]	$r_{Cu_1-Se_5}$ [pm]	$r_{Cu_3-Se_5}$ [pm]	$r_{Cu_1-Cu_2}$ [pm]	$r_{Cu_3-Cu_4}$ [pm]	$r_{Cu_1-Cu_3}$ [pm]
SCF	D	227.5	245.2	480.3	239.6	347.0
MP2	D	222.8	237.0	261.2	221.6	260.2
LDF	DNP[b]	224.5	238.8	245.4	235.1	254.3
CCSD(T)	D	225.1	240.5	256.7	226.1	263.9
SCF + Δg[c]	D	222.6	240.0	242.0	220.0	251.6
SCF + Δg[d]	D	223.1	240.2	280.1	227.3	277.8

[a] as described in Table 1
[b] Double numeric with polarization functions
[c] ε_2, Eq. (1)
[d] ε_3, Eq. (4)

leading to further stabilization. For the C_{2h} and D_{4h} isomers the geometry changes due to correlation effects are much less pronounced. In these two isomers either Cu has direct interactions with two Se, especially in the D_{4h} structure, and the arrangement of the Cu atoms is therefore more rigid (even on the SCF level).

The energetic ordering of the three dimers is in line with the amount of Cu aggregation. The number of 'close' Cu–Cu distances (i.e. $r_{CuCu} < 270$ pm) is 4 for the D_{4h}, 5 for the C_{2h} and 6 for the C_{2v} structure. This indicates that Cu aggregation is an important driving force for the formation of $(Cu_2Se)_n$ clusters.

Table 5. Geometries obtained for the C_{2h} isomer of Cu_4Se_2

Method	Basis[a]	$r_{Cu_1-Se_5}$ [pm]	$r_{Cu_3-Se_5}$ [pm]	$r_{Cu_1-Cu_3}$ [pm]	$r_{Cu_3-Cu_4}$ [pm]
SCF	D	228.6	245.0	317.0	239.8
MP2	D	223.4	236.6	258.8	221.2
LDF	DNP[b]	224.6	239.0	244.3	237.3
CCSD(T)	D	225.5	240.1	259.8	225.8
SCF + Δg[c]	D	229.7	237.4	236.4	227.8
SCF + Δg[d]	D	226.8	239.0	255.4	232.8

[a] as described in Table 1
[b] Double numeric with polarization functions
[c] ε_2, Eq. (1)
[d] ε_3, Eq. (4)

Table 6. Geometries obtained for the D_{4h} isomer of Cu_4Se_2

Method	Basis[a]	r_{CuSe} [pm]	r_{CuCu} [pm]
SCF	C	256.9	246.5
	D	254.1	239.8
MP2	C	247.3	231.0
	D	245.8	222.8
LDF	DNP[b]	247.1	230.0
CCSD(T)	D	249.1	224.6
SCF + Δg[c]	D	247.2	223.7
SCF + Δg[d]	D	248.2	228.6

[a] as described in Table 1
[b] Double numeric with polarization functions
[c] ε_2, Eq. (1)
[d] ε_3, Eq. (4)

Table 7. Relative stabilities of the three isomers of Cu_4Se_2. Energies are given in kJ/mol and refer to calculations with basis DNP for LDF and basis D for the other methods at respective equilibrium structures

Method	C_{2v}	C_{2h}	D_{4h}
SCF	0	− 14.6	+ 17.9
MP2	0	+ 6.6	+ 23.7
LDF	0	+ 17.7	+ 26.5
CCSD(T)	0	+ 4.9	+ 13.6

5 The SCF + Δg approach

In a previous treatment of binuclear and trinuclear copper clusters [2], it has been demonstrated that a simple modelling of correlation corrections added to SCF energies can greatly improve results of computed structure constants. In the course of this work we have investigated the usefulness of two different approximations for the dependence of the correlation energy on the structure. The simpler ansatz ε_2 involves only two-body terms describing Cu–Cu and Cu–Se interactions:

$$E_{corr} \approx \varepsilon_2 = \sum_{i<j} f(r_{ij}) + \sum_{i,k} g(r_{ik}) \tag{1}$$

where i, j and l always label Cu atoms and k the Se atoms. The functions f and g have been fitted to CCSD(T), basis D, correlation energies of Cu_2Se in the following way:

$$f(r) = -0.632 - 0.184{*}\exp(-0.423{*}r)\ [\text{a.u.}] \tag{2}$$

$$g(r) = -0.322 - 1.441{*}\exp(-1.293{*}r)\ [\text{a.u.}] \tag{3}$$

This analytic form was chosen – among others involving e.g. r^{-n} – since it is simple and has a reasonable asymptotic behaviour for large r.

The addition of ε_2 to the SCF energy reproduces the CCSD(T) structure constants of Cu_2Se (basis D) within 0.1 pm and 0.1° (Table 3). This confirms sufficient quality of the fits, and also that couplings of the Cu–Cu and Cu–Se distances are of negligible importance (as had been checked beforehand, of course).

The use of ε_2 to correct SCF energies leads to a marked improvement of structure constants for the D_{4h} isomer of Cu_4Se_2 (Table 6): deviations to CCSD(T) are less than 2 pm (up to 21.9 pm for SCF!). The performance for the C_{2v} and C_{2h} structures is much less satisfactory, however, with deviations of up to 23.4 pm (Cu_1–Cu_3 in C_{2h}, Table 5), and 14.7 pm (Cu_1–Cu_2 in C_{2v}, Table 4). This failure was attributed to three-body correlation interactions of Cu atoms. This lead to the second ansatz ε_3 to describe correlation effects:

$$E_{corr} \approx \varepsilon_3 = \varepsilon_2 + \sum_{i<j<l} h\left(\frac{r_{ij} + r_{il} + r_{jl}}{3}\right), \tag{4}$$

where the sum runs over all triples of Cu atoms. This is the simplest way to account for three-body correlation contributions since it involves only the totally symmetric term, i.e. the circumference of the corresponding Cu triangle. For h we have put:

$$h(r) = const + 0.931{*}\exp(-0.959{*}r)\ [\text{a.u.}]. \tag{5}$$

The constant has not been fixed since it contains superfluous contributions which vanish in the gradient. This choice emerged from CCSD(T) trial calculations on Cu_3As (C_{3v} symmetry), the closest analogue to Cu_2Se which displays three-body Cu interaction, and from trial calculations for the local minima of the potential surface of Cu_4Se_2.

The inclusion of the three-body term leads to slightly poorer structure constants for the D_{4h} structure (deviation of 4 pm for Cu–Cu in comparison to CCSD(T)), but to much better agreement for C_{2h} (largest deviation now 7 pm for Cu_3–Cu_4, as compared to 23.4 pm for Cu_1–Cu_3 if only ε_2 is included). The three-body Cu interaction term h also leads to closer agreement of Cu–Se distances with CCSD(T) results for all structures with deviations typically reduced by a factor of two. For the C_{2v} structure there are still large discrepancies in the Cu–Cu distances (largest deviation is 23.4 pm for the 'floppy' Cu_1–Cu_2 distance), although the Cu_3–Cu_4 distance is now reproduced within 1 pm. This may be rationalized by two aspects: there are in part very small force constants since the Cu substructure is not held together as tightly as in the other isomers (see last section), and the Cu atoms form a distorted tetrahedron so that even four-body interactions might be important. We did not include four-body interactions in our model in order not to push the approximation too far.

6 Concluding remarks

Cu_2Se and its dimer (and according to preliminary investigations also the trimer) show a pronounced tendency to form Cu aggregations as indicated by Cu–Cu distances as small as around 225 pm. For comparison we note the equilibrium distance of 222 pm in Cu_2 [18] and, according to high level calculations (CPF including relativistic effects), of 216 pm in Cu_2H_2 (D_{2h}) [2]. In both cases there is clearly direct Cu–Cu bonding, whereas the probably shortest known non-bonding distance of 235 pm occurs in $[CuN_5R_2]_3$ [2]. This state of affairs strongly suggests direct Cu–Cu bonding contributions in $(Cu_2Se)_n$ and leads to the question: Can the Cu_4 aggregates in Cu_4Se_2 be considered as copper-clusters which are partially oxidized by outer selenium atoms? The results of population analyses – though limited in reliability – lend support to the idea of 'metal' cages. The atomic charges (+ 0.3 to + 0.4 for Cu) as well as Cu–Se SEN (0.4 to 1.0) are consistent with the idea of polar Cu–Se bonds. In all cases there is further evidence of direct CuCu-bonding: The two-center SENs are 0.1 to 0.3, the largest three-center SEN is 0.1 in the C_{2v} isomer and the largest four-center SEN is 0.4 in the D_{4h} isomer (this is normally only found for molecules with delocalized electron systems such as benzene). Whereas the α-phase of solid Cu_2Se is a semiconductor, the present results do not exclude metal-cluster-type behaviour of $(Cu_2Se)_n$ clusters. This aspect will be further analyzed in calculations involving larger clusters and their properties such as polarizability or electronic excitations.

Inclusion of dynamic electron correlation is essential for a correct description of the geometries of $(Cu_2Se)_n$ clusters. Of all methods applied we consider CCSD(T) to be most reliable. The energetic separation of only 4.9 and 8.7 kJ/mol between the isomers of Cu_4Se_2 obtained with this method certainly implies $(Cu_2Se)_n$ to be demanding systems. Of all methods applied, MP2 and LDF give the same energetic ordering as CCSD(T). MP2 structure parameters are also in satisfactory to tolerable agreement with those from CCSD(T): Cu–Se distances deviate by at most 3.5 pm (MP2 too short throughout, as for Cu_2Se), whereas Cu–Cu distances differ by at most 4.6 pm (deviations in either direction). The SCF approximation clearly is of little use both for relative energies (wrong order of isomers) as for structure constants (even for the simplest case, D_{4h}, the Cu–Cu distances, SCF versus CCSD(T), differ by 21.9 pm, deviations are partly much larger for the other isomers, especially for C_{2v}).

The LDF results are roughly in-between SCF and CCSD(T). LDF yields the same energetic ordering as CCSD(T) but structure constants differ markedly. Cu–Cu distances for the relatively stiff D_{4h} structure differ from CCSD(T) by 5.4 pm, for the C_{2h} structure they are 11.5 pm too long (Cu_3–Cu_4) and 14.5 pm too short (Cu_1–Cu_3), whereas deviations scatter around 10 pm for C_{2v}. Recently developed nonlocal, gradient-corrected density functionals [19] might reduce the discrepancies, but with these the advantage in computation time compared to MP2 is partly lost.

The SCF + Δg method has proved applicable, except in special cases involving very floppy modes. With inclusion of the simplest ansatz for three-body interactions the CCSD(T) structure constants of the D_{4h} and C_{2h} isomers are reproduced within 7 pm for Cu–Cu distances and 1.3 pm for Cu–Se distances. For the C_{2v} structure the deviations from CCSD(T) are up to 23.4 pm for Cu–Cu distances but still relatively small compared to the SCF results. LDF and SCF + Δg are at least viable methods for exploring the energy surfaces of larger clusters, e.g. to get starting geometries for a subsequent MP2 treatment.

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References

1. Fenske D, Krautscheid H (1990) Angew Chem 102:1513
2. Kölmel CM, Ahlrichs R (1990) J Phys Chem 94:5536
3. Møller C, Plesset MS (1934) Phys Rev 46:618
4. Ahlrichs R, Bär M, Häser M, Horn H, Kölmel C (1989) Chem Phys Letters 162:165; Haase F, Ahlrichs R (1993) J Comp Chem 14:907
5. Purvis GD, Bartlett RJ (1982) J Chem Phys 76:1910
6. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) Chem Phys Letters 157:479
7. Stanton JF, Gauss J, Watts JD, Lauderdale WJ, Bartlett RJ (1991) ACES II, Univ of Florida, Gainesville
8. Ahlrichs R, Scharf P, Ehrhardt C (1985) J Chem Phys 82:890
9. Lischka H, Shepard R, Brown FB, Shavitt I (1981) Int J Quantum Chem Symp 15:91, Shepard R, Shavitt I, Pitzer RM, Comeau DC, Pepper M, Lischka H, Szalay PG, Ahlrichs R, Brown FB, Zhao JG (1988) Int J Quantum Chem Symp 22:149
10. Hohenberg P, Kohn W (1964) Phys Rev B 136:864; Kohn W, Sham LJ (1965) Phys Rev A 140:1133
11. Delley B (1990) J Chem Phys 92:508
12. Dolg M, Wedig U, Stoll H, Preuss H (1987) J Chem Phys 86:866
13. Hurley MM, Pacios LF, Christiansen PA, Ross RB, Ermler WC (1986) J Chem Phys 84:6840
14. Schäfer A, Horn H, Ahlrichs R (1992) J Chem Phys 97:2571
15. Davidson ER (1967) J Chem Phys 46:3320; Roby KR (1974) Mol Phys 27:81
16. Ehrhardt C, Ahlrichs R (1985) Theoret Chim Acta 68:231
17. Wadt WR, Hay PJ (1985) J Chem Phys 82:284
18. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure, Vol 4. Van Nostrand, NY, p 198
19. Becke AD (1992) J Chem Phys 96:2155 and references therein